## **Reactions of Cyclic Boric Acids Esters with Paraformaldehyde**

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**Abstract**—Reactions of five- and six-membered cyclic esters of boric acids with paraformaldehyde lead to the corresponding 1,3-dioxacycloalkanes. It is shown that *trans*-isomers of 2,4,5-substituted 1,3,2-dioxaborinanes react faster than their *cis*-isomers.

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One of the promising directions in chemistry of cycloalkane heteroanalogs is connected with the revealing the possibility of mutual transformations of compounds of different classes. In particular, the reaction of acyclic organoboron compound with 1,3dioxa- as well as with 1,3-dioxa-2-heterocycloalkanes containing silicon, sulfur, germanium, and arsenic atoms in the position 2 of the ring leads to corresponding 1,3-dioxa-2-boronocycloalkanes. The reverse process is also possible. The reaction of carbonyl compounds with 1,3-dioxa-2-boronocycloalkanes leads to the deborination of heterocyclic system and the formation of the corresponding 1,3dioxacycloalkanes. We have shown recently that the reaction of substituted 1,3,2-dioxaborinanes with paraformaldehyde, as well as with acetic, propionic, and isobutyric aldehydes yields the corresponding dioxanes [2-5]. Here we report on further studies of the reaction of five- and six-membered cyclic esters of boric acids Ia-XIIa with paraformaldehyde.

It is established that the reaction under investigation leads to the corresponding 1,3-dioxolanes and 1,3dioxanes **Ib–XIIb**. It takes place while heating a mixture of starting substances in the presence of a catalytic amount of zinc chloride. Yields of lowboiling products **Ib–VIIIb** vary from 24 to 82% (see Table 1). No unambiguous dependence of the yield on the degree of substitution of the ring, on the size of the cycle, and on the number of carbon atoms in the alkoxy substituent at the boron atom was found.



Data of Table 2 show that the conversion of cyclic boric esters to the corresponding 1,3-dioxanes is not high. According to GLC data it does not exceed 30%. After 8 h since the start of the reaction the products, formals Xb and XIb, have higher content of *trans*-form as compared to the expected results. Inasmuch as the formation of cyclic boric esters and 1,3-dioxanes from stereoisomeric 1,3-diols proceeds stereospecifically [6-8], these data show the difference in the rate of the reactions of cis- and trans-isomers of compounds Xa and XIa with paraformaldehvde. The ratio of isomers in the samples of 1,3-dioxanes obtained by an independent synthesis from the corresponding 1,3-diols and paraformaldehyde was taken as standard [8, 9]. In the case of ester Xa and 1,3-dioxane Xb the samples with different ratio of cis- and trans-forms were studied [9, 10].

Note that 1,3,2-dioxaborinanes **Xa**, **XIa** are configurationally stable. They do not isomerize under

Boric esters	R	$\mathbf{R}^1$	$\mathbb{R}^2$	Yield, %	
Ia	C <sub>4</sub> H <sub>9</sub>	Н	Н	77	
IIa	$i-C_5H_{11}$	Н	Н	24	
IIIa	$C_{6}H_{13}$	Н	Н	27	
IVa	$C_7H_{15}$	Н	Н	31	
Va	i-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	Н	82	
VIa	$C_{7}H_{15}$	$CH_3$	Н	53	
VIIa	i-C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>	30	
VIIIa	_	_	_	36	

 Table 1. Yield of 1,3-dioxacycloalcanes Ib–VIIIb in the reactions of cyclic boric esters Ia–VIIIa with paraformaldehyde

the action of zinc chloride [5, 6]. Hence, considering the accuracy of GLC measurements ( $\pm 3\%$ ) [11], the rate of the reaction of *trans*-form of cyclic boric esters **Xa**, **XIa** with paraformaldehyde is higher than that of the *cis*-form leading to the increase in the content of *trans*-isomers of 1,3-dioxanes **Xb**, **XIb** at the end of the controlled period. It agrees with the known data that the rate of borination, the reversed reaction, in the case of *cis*-isomer of dioxane **Xb** is higher than that of the corresponding *trans*-form [9].

$$C_{6}H_{5} - \underbrace{\bigcirc}_{O}^{O}B - i \cdot C_{3}H_{7} \xrightarrow{(CH_{2}O)_{n}, ZnCl_{2}}_{-(i \cdot C_{3}H_{7}BO)_{3}} C_{6}H_{5} - \underbrace{\bigcirc}_{O}^{O}$$

$$IXa IXb$$

$$R - \underbrace{\bigcirc}_{O}^{O}B - i \cdot C_{4}H_{9} \xrightarrow{(CH_{2}O)_{n}, ZnCl_{2}}_{-(i \cdot C_{4}H_{9}BO)_{3}} R - \underbrace{\bigcirc}_{O}^{O}$$

$$H_{3}C$$

$$Xa - XIa Xb - XIb$$

$$R = i \cdot C_{3}H_{7} (X), C_{6}H_{5}CH_{2} (XI).$$

$$H_{3}C - \underbrace{\bigcirc}_{O}^{O}B - i \cdot C_{4}H_{9} \xrightarrow{(CH_{2}O)_{n}, ZnCl_{2}}_{-(i \cdot C_{4}H_{9}BO)_{3}} H_{3}C - \underbrace{\bigcirc}_{O}^{O}$$

$$XIIa XIIb$$

Molecules of the ester **XIIa** are configurationally unstable and relatively easily isomerize under the action of catalytic amounts of  $ZnCl_2$  giving the more stable *trans*-isomer [6, 12].

It may be suggested that due to that the approach of the aldehyde molecule from the side of more reactive  $O^3$  oxygen atom is complicated decreasing the activity of borinane **XIIa** in the reaction with paraformaldehyde.

 $\frac{1,3-\text{dioxanes }(b)}{cis:trans}$ 

	Conversion	cis:trans					
Boric		а	b	after 8 h			
esters	degree, %	(before	(counter	4	h		
		reaction)	synthesis)	и	υ		
IXa	30	_	_	-	-		
Xa	25	77:23	67:33	88:12	62:38		
		35:65	39:61	48:52	33:67		
XIa	20	66:34	66:34	68:32	57:43		
XIIa	1	83:17	80:20	26:74	-		

Table 2. Conversion of 1,3,2-dioxaborinanes IXa-XIIa and



Note that the reverse reaction, borination of 1,3dioxanes with the acyclic boric esters under the analogous conditions leads to the preferred formation of the target 1,3,2-dioxaborinanes [9, 13]. Hence, it is thermodynamically more favorable.

## **EXPERIMENTAL**

GLC analysis was carried out on a Tsvet-126 chromatograph equipped with the flame ionization detector and the 3000×4 mm column filled with 5% of OV-17 on the Chromaton N-Super carrier, carrier gas argon. Quantitative ratio of 1,3,2-dioxaborinane and 1,3-dioxane was evaluated by means of the internal reference method with the calibrating coefficients established according to the procedure [11].

Boric esters **Ia–XIIa** were obtained by the reaction of acyclic trialkyl borates or the esters of isopropyl- or isobutylboric acids with the corresponding 1,2 and 1,3diols according to the general procedure [14]. The independent synthesis of 1,3-dioxanes **IXb–XIIb** is described in [8, 9, 15]. 1,3-Dioxacycloalkanes **Ib-XIIb** were identified by their physicochemical constants [15, 16]. Samples of 2-isopropyl-1,3-butanediol with the varied ratio of *erythro-* and *treo*-forms necessary for preparing model compounds, boric ester **Xa** and 1,3dioxane **Xb**, were obtained according to the procedures [8, 17, 18].

In the case of preparative isolation of 1,3dioxacycloalkanes a mixture of 0.1 mol of cyclic boric ester **Ia–VIIIa**, 0.5 mol of paraformaldehyde, and 0.7 g of anhydrous zinc chloride was heated to 130–150°C and the target low-boiling product was distilled off. In the analytic procedures a mixture of 0.01 mol of boric ester **IXa–XIIa**, 0.05 mol of paraformaldehyde, and 0.5 g of the anhydrous ZnCl<sub>2</sub> was heated at 130°C for 8 h with the intermittent sampling for GLC analysis.

## REFERENCES

- Kuznetsov, V.V., *Khim. Geterotsikl. Soedin.*, 2006, no. 5, p. 643.
- 2. Kuznetsov, V.V. and Gren', A.I., Zh. Obshch. Khim., 1963, vol. 33, no. 6, p. 1432.
- Kuznetsov, V.V., *Khim. Geterotsikl. Soedin.*, 2001, no. 1, p. 136.
- Kuznetsov, V.V. and Brusilovskii, Yu.E., Abstract of Papers, XX Ukrane Conf. on Organic Chemistry, Odessa, 2004, p. 235.
- Kuznetsov, V.V., Zh. Org. Khim., 2001, vol. 37, no. 9, p. 1423.
- 6. Kuznetsov, V.V., Alekseeva, E.A., and Gren', A.I., *Khim. Geterotsikl. Soedin.*, 1995, no. 9, p. 1291.
- Kuznetsov, V.V., Bochkor, S.A., and Spirikhin, L.V., Bashk. Khim. Zh., 2000, vol. 7, no. 5, p. 23.

- Bogastskii, A.V., Samitov, Yu.Yu., Gren', A.I., and Soboleva, S.G., *Khim. Geterotsikl. Soedin.*, 1971, no. 7, p. 893.
- Kuznetsov, V.V., *Khim. Geterotsikl. Soedin.*, 2002, no. 8, p. 1149.
- 10. Kuznetsov, V.V., *Khim. Geterotsikl. Soedin.*, 2002, no. 10, p. 1453.
- Vyakhirev, D.A. and Shushunova, A.F., *Rukovodstvo po gazovoi khromatografii* (Handbook of Gas Chromatography), Moscow: Vysshaya Shkola, 1975, p. 129.
- 12. Kuznetsov, V.V. and Spirikhin, L.V., Zh. Strukt. Khim., 2000, vol. 41, no. 4, p. 844.
- 13. Kuznetsov, V.V., Tereshchenko, A.V., and Gren', A.I., *Zh. Obshch. Khim.*, 1996, vol. 66, no. 2, p. 270.
- 14. Gren', A.I. and Kuznetsov, V.V., *Khimiya tsiklicheskikh efirov bornykh kislot* (Chemistry of Cyclic Boric Acid Esters), Kiev: Naukova Dumka, 1988.
- Rakhmankulov, D.L., Syrkin, A.M., Karakhanov, R.A., Kantor, E.A., Zlotskii, S.S., and Imashev, U.B., *Fizikokhimicheskie svoictva 1,3-dioksanov* (Physicochemical Properties of 1,3-Dioxanes), Moscow: Khimiya, 1980.
- Elderfield, R. and Short, F.V., *1,3-Dioksolany. Geterotsiklicheskie soedineniya* (1,3-Dioxolanes. Heterocyclic Compounds), Elderfield, R., Ed., Moscow: Inostrannaya Literatura, 1961, vol. 5, no. 7.
- Bogatskii, A.V., Samitov, Yu.Yu., Gren, A.I., and Soboleva, S.G., *Tetrahedron*, 1975, vol. 31, no. 6, p. 489.
- Bogatskii, A.V., Luk'yanenko, N.G., Lyamtsev, a L.N., Teterina, T.G., and Vasilova, I., *Zh. Org. Khim.*, 1981, vol. 17, no. 6, p. 1202.